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THE EFFECT OF VENTILATION ON EMISSION RATES OF WOOD FINISHING MATERIALS

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16. ABSTRACT The paper gives results from EPA studies on the effect of ventilation (air changes per hour) and material loading on the emission rate for selected organics and total measured organics from three wood finishing materials (stain, polyurethane, and wax). The data are analyzed to show the effect of ventilation on the emission characteristics of each material. The rate of emission of organic compounds from building materials varies according to: type of material, material loading (area of material/volume of room), compound emitted, temperature, humidity, and ventilation rate. For some compounds and materials (e.g., formaldehyde from particleboard), the relationship between emission rate and these variables is well established. For most materials and compounds, however, such relationships are unavailable. Research, using small test chambers, is being conducted by EPA to develop data on emission rates from a variety of building materials.

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Abstract

The rate of emission of organic compounds from building materials varies according to: type of material, material loading (area of material/volume of room), compound emitted, temperature, humidity, and ventilation rate. For some compounds and materials (e.g., formaldehyde from particleboard), the relationship between emission rate and these variables is well established. For most materials and compounds, however, such relationships are unavailable. Research, using small test chambers, is being conducted by the U.S. Environmental Protection Agency (EPA) to develop data on emission rates from a variety of building materials. This paper presents selected results from the EPA studies. Emphasis is placed on the effect of ventilation (air changes/hour) and material loading on the emission rate for selected organics and total measured organics. Test data for three wood finishing materials (i.e., stain, polyurethane, and wax) are presented. The data are analyzed to show the effect of ventilation on the emission characteristics of each material.

Introduction

The rate of emission of organic compounds from building materials varies according to: type and age of material, material loading (area of material/volume of room), compound emitted, temperature, humidity, and ventilation rate (9). Numerous studies have been conducted on emissions of formaldehyde from pressed wood products, and relationships between the emission rate and the controlling variables have been established (4, 5, 7). Studies have also been conducted on emissions of a variety of organic compounds from various building materials and consumer products (2, 3, 6, 9). Such studies are generally conducted under constant environmental conditions, and while they provide emission rate data (e.g., mg/m^2-hr), they do not generally examine the effect of the controlling variables on the emission rate.

When emissions from materials are evaporative, the effect of ventilation (air exchange rate) is well understood. As the air exchange rate increases, the indoor concentration decreases due to dilution and flushing. This reduced concentration increases the difference in vapor pressure between the emission source and the indoor environment. Since the vapor pressure difference is the driving force for evaporation, the emission rate increases. Thus, higher air exchange rates cause higher emission rates. Material loading has the opposite effect; as the loading is increased, the concentration increases and the vapor pressure difference decreases. This decreases the emission rate. Thus, for evaporative emissions, the emission rate is generally proportional to the ratio of the air exchange rate (N) and material loading (L). This relationship has been shown for formaldehyde emissions from particleboard (4, 5, 7).

In some cases, where the emission rate is not purely evaporative, diffusion of the emitting compound within the source may be important. If the diffusion of the compound to the surface of the source is slower than the evaporation rate, then the rate of emission will be reduced. If the diffusion rate is very slow, changing the air exchange rate will have minimal effect on the emission rate. One study suggests that non-formaldehyde emissions from particleboard are diffusion limited (7).

Finally, the effect of sinks in the indoor environment can affect the emission rate. As compounds are emitted, they may adsorb to other materials. Such adsorption causes a decrease in concentration analogous to an increase in air exchange rate. The effect on emission rate is similar; that is, a sink effect can cause an increase in the emission rate.

The United States Environmental Protection Agency is conducting research on the processes affecting the rate of emission of organic compounds from building materials and consumer products (8). Studies are being conducted on dry, constant emission (or slowly decaying) sources (e.g., particleboard, moth crystal cakes) and on wet, decreasing emission sources (e.g., caulks, adhesives, paints, waxes). Previous papers have discussed the results of this research (7, 8, 9), including the development of a source emissions model which accounts for effects of vapor pressure and sinks on emission rates for the chamber experiments (1). This paper presents results of experiments to determine the effect of air exchange rate and material loading on emissions of organic compounds from three materials: wood stain, polyurethane wood finish, and liquid wood floor wax. The materials tested are commonly available and were purchased at a local retail store.

Experimental procedures

Laboratory facility

EPA's Indoor Air Source Characterization Laboratory consists of: a clean air conditioning and delivery system, an incubator containing two 166 liter environmental test chambers, sampling manifolds, and sample collection adsorbers using Tenax and charcoal. A fan in each chamber ensures complete mixing. A permeation system for quality control is included. The environmental variables are monitored and controlled by a microcomputer. Organic analyses are conducted by thermal desorption, concentration via purge and trap, and gas chromatography (GC) using flame ionization detectors (FID). A separate microcomputer provides GC data analysis. All data are input to spreadsheets for further analysis.

Headspace analysis

Prior to evaluation in the environmental test chambers, materials are evaluated by headspace analysis. A sample of material is placed in a 1 liter Teflon-lined container that is purged with nitrogen at 50 ml/min for 30 min. The exit flow is collected on Tenax and analyzed after thermal desorption. Gas chromatography/mass spectroscopy (GC/MS) analysis identifies the compounds contained in the material's emissions. Approximately 10 of the compounds of highest concentration are selected for measurement in subsequent chamber tests. Table 1 shows the compounds selected for the stain, polyurethane, and wax, based on GC/MS analysis.

Table 1. Compounds identified by headspace analysis.

Material	Compounds
Wood stain	2-butanone, benzene, hexane (isomer), trimethylhexane (two isomers), nonane, decane (two isomers), cyclodecane (isomer), trimethylbenzene, n-decane, undecane
Polyurethane	ethylbenzene, nonane, trimethylbenzene, n-decane, undecane, hexanal*
Wood floor wax	trimethylcyclohexane, methyloctane, methylethylcyclohexane (two isomers), nonane, dimethyloctane, p-ethyltoluene, trimethylbenzene, n-decane, undecane

*Hexanal was not identified in the original headspace analysis; it was discovered several hours after chamber testing began and was identified by subsequent GC/MS analysis after collection on XAD.

Chamber testing

Experimental designs were established for each material tested to evaluate the effect of various parameters: temperature, air exchange rate (N), and chamber loading (L). For the materials discussed herein, all testing was conducted at 50% relative humidity. The stain and polyurethane were tested at 23°C; the wax at 20°C. Table 2 provides the test matrices showing N, sample area (A), and L for the three materials. The number of test replicates is also shown.

Table 2. Chamber test conditions.

Material	N (hr^{-1})	A (cm^2)	L (m^2/m^3)	N/L	No. of Reps.
Wood stain	0.35	2158	1.3	0.27	2
	0.35	166	0.1	3.50	1
	2.5	1162	0.7	3.57	2
	4.6	2158	1.3	3.54	2
Polyurethane	0.5	347	0.21	2.38	2
	1.0	694	0.42	2.38	2
	1.0	347	0.21	4.76	2
	2.0	347	0.21	9.52	2
Wood floor wax	0.25	200	0.12	2.1	1
	0.5	200	0.12	4.2	2
	0.5	100	0.06	8.3	1
	1.0	200	0.12	8.3	1
	2.0	400	0.24	8.3	1
	2.0	200	0.12	16.7	1

Prior to each test, the chambers were purged with clean air for several hours before placing samples in the chambers. The sample substrates varied according to the material being tested. The wood stain was applied to hardwood (poplar) boards that had their edges sealed with sodium silicate; the polyurethane was applied to the stained boards; the floor wax was spread on aluminum plates. [Note that the floor wax was tested prior to the other two materials. The aluminum plate substrate was selected to make the testing consistent with other materials (i.e., caulk, flooring adhesive) tested in the chambers.] The samples were placed in the chamber shortly after the material was applied to the substrate. The test start (time = 0) was established when the door to the chamber was closed. The first sample was collected within 30 min. of the start. The samples were collected on Tenax/charcoal and analyzed by GC/FID. Throughout the test, an internal standard (usually hexane) was added from the permeation ovens for quality control. The organic species quantified depended on the

results of the headspace analysis; total measured organics (as hexane) were also determined and recorded. The duration of each test depended on the type of material being tested; generally, tests were concluded when the same chamber concentration was observed for several measurements or when the analytical detection limits were reached.

Chamber data

The results of the chamber testing are illustrated in Figure 1 where the concentration of total organics and four individual compounds is presented for the wood stain tested at an air exchange rate (N) of 0.35 hr^{-1} and a sample area (A) equal to 166 cm^2. Data are presented for the first day of a 7 day test. The concentration of total organics at the end of the test was less than 1 mg/m^3. The figure shows the concentration increasing rapidly for the first 1 or 2 hours and then declining as the emission rate drops and the material is diluted and flushed from the chamber. This behavior is typical of wet, solvent-containing materials.

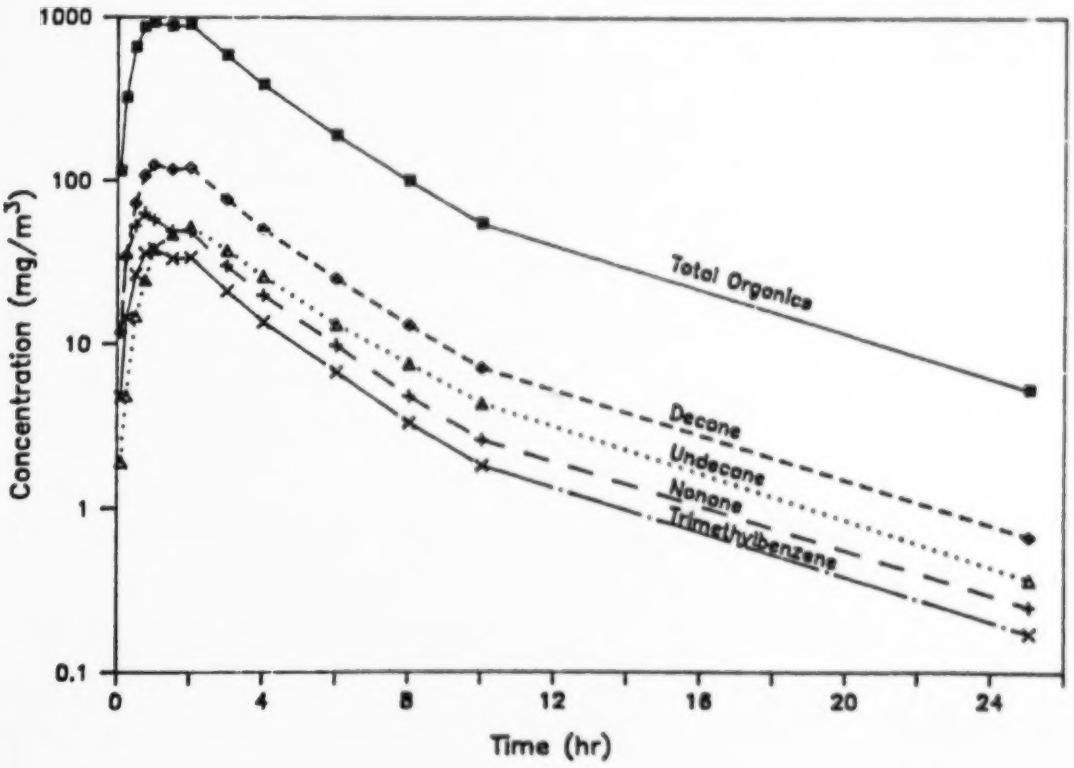

Fig. 1 Chamber data -- wood stain.

Data analysis

Models have been developed to analyze the results of the chamber tests in order to provide emission rates (1). The simplest model (i.e., neglecting sink and vapor pressure effects) assumes: a) the chambers are ideal continous stirred tank reactors (CSTR), and b) the change in emission rate can be approximated by a first order decay, as shown in equation 1.

$$R = R_o e^{-kt} \quad (1)$$

Where, R = Emission rate, mg/m^2-hr
R_o = Initial emission rate, mg/m^2-hr
k = First order rate constant, hr^{-1}
t = Time, hr
e = Natural log base

The mass balance for the chamber over a small time increment dt is:

Change in mass = Mass emitted - Mass leaving chamber

This can be express as:

$$VdC = AR_o e^{-kt}dt - QCdt \quad (2)$$

Where, V = Chamber volume, m^3
C = Chamber concentration, mg/m^3
A = Area of source, m^2
Q = Flow through chamber, m^3/hr

Equation 2 can be rearranged:

$$dC/dt + (Q/V)C = (A/V)R_o e^{-kt} \quad (3)$$

Equation 3 is a linear, non-homogeneous differential equation. Given that C = 0 when t = 0, the solution to equation 3 is:

$$C = AR_o(e^{-kt} - e^{-Nt})/V(N - k) \quad (4)$$

Where, N = Air exchange rate, hr^{-1}, and is equal to Q/V

Using a non-linear regression curve fit routine, implemented on a microcomputer, values of R_o and k can be obtained by fitting the concentration vs. time data from the chambers to equation 4. In order to conduct such analyses, initial estimates of R_o and k are required. A good initial estimate of k is:

$$k = Ne^{(k-N)tmax} \quad (5)$$

Where, tmax is the time of maximum concentration (Cmax).

Equation 5 is obtained by substituting C (equation 4) into equation 3 and setting $dC/dt = 0$ at $t = t_{max}$. Once an estimate of k is achieved from equation 5, R_o can be estimated from equation 4. Figure 2 illustrates the curve fitting process for a wood stain chamber test; the solid line is the "best fit" of equation 4, and the data points are shown as diamonds. (Figure 2 shows only the first 10 hr of data, but the fit was made over the total test period.)

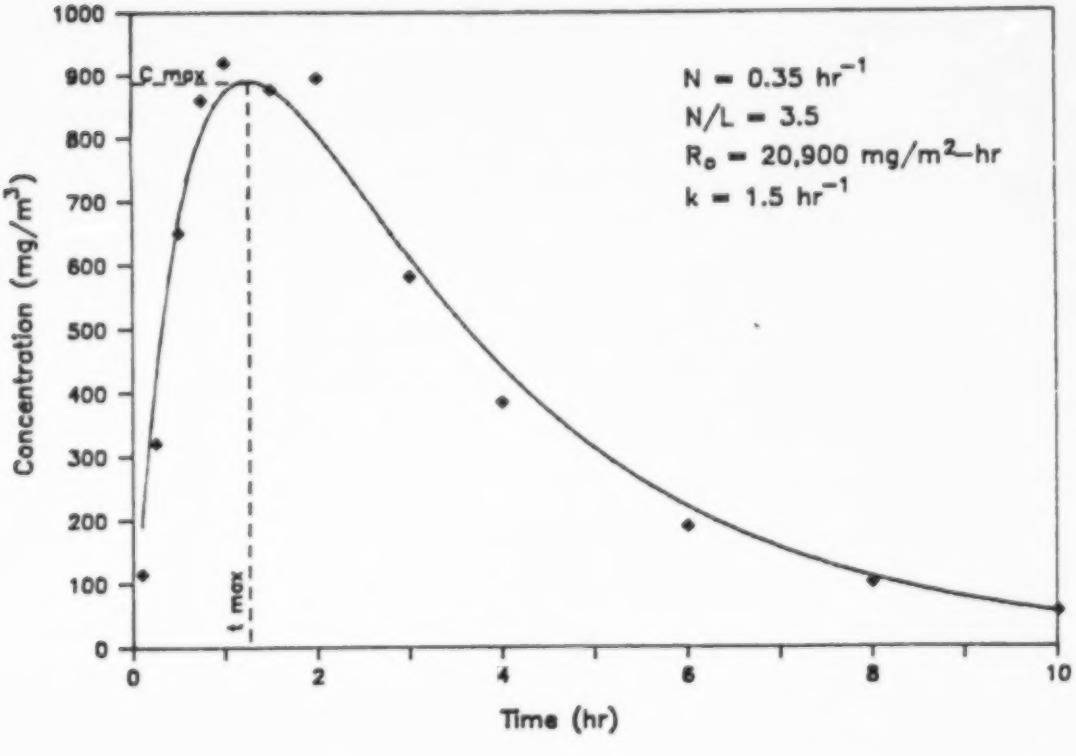

Figure 2. Wood stain -- total organics.

All of the test runs were analyzed using this procedure, and the results (R_o and k) for total organics are presented in Table 3. The table also contains values for R_o/k, which represents the total available emissions (or source strength) per unit area for the material being tested. Total emissions are estimated by integrating equation 1 from time zero to infinity. Each row in Table 3 corresponds to the test conditions for the same row in Table 2.

Table 3. Results of data analyses.

Material	N/L	R_o (mg/m^2-hr)	k (hr^{-1})	R_o/k (mg/m^2)
Wood stain	0.27	2200	0.24	9200
	3.50	20900	1.51	13800
	3.57	17400	1.24	14000
	3.54	27000	2.41	11200
Polyurethane	2.38	1680	0.25	6720
	2.38	2610	0.29	9000
	4.76	6500	0.61	10660
	9.52	5780	0.64	9480
Wood floor wax	2.1	38000	6.3	6030
	4.2	23000	5.3	4340
	8.3	19000	5.4	3520
	8.3	28000	10.2	2750
	8.3	32000	8.1	3950
	16.7	23000	6.3	3650

Discussion of results

The values of R_o and k allow comparisons of the emissions characteristics of the materials between test conditions. The N/L ratio is used to investigate the effect of ventilation on the emission characteristics. For a given L, any change in N/L is directly proportional to the air exchange rate (N). The wood stain results show a clear effect of N/L, where the three tests with similar N/L values (i.e., 3.50, 3.57, and 3.54) have consistent R_o and k values. The test with the low N/L has much lower values for R_o and k. This indicates that, for the low N/L test, vapor pressure suppression is occurring which causes a reduction in the initial emission rate and a much slower decay. Note that the R_o/k values are consistent for all four tests, indicating that the total emissions (mg/m^2) were similar. The data for polyurethane also show vapor pressure suppression, since the R_o and k values for the tests conducted at N/L = 2.38 are lower than for the other two test conditions. Note that there is little difference between the R_o and k values for the tests with N/L = 4.76 and 9.52. This may indicate that, at higher N/L values, diffusion limitations may be occurring. The results of the wood floor wax testing show little relationship between the N/L values and the R_o and k values. Under all test conditions, the emission rate was extremely fast. The average k = 6.7 hr^{-1}, which indicates that 95% of the emissions occurred within the first 30 minutes. Thus, in a practical sense, the emissions from the wood floor wax can be considered to occur in a single burst with essentially no emissions occurring after the first few minutes of application.

The results can also be used to compare the emission characteristics of the three materials. In terms of emission rates, the wood floor wax has the highest initial rate (R_o) and the fastest decay (k); the wood stain also has a high initial emission rate, but a much slower decay; the polyurethane finish has the lowest initial emission rate and the slowest decay.

The source strengths (or total available emissions) from the materials can be compared, using the R_o/k ratio. Table 4 shows the source strengths, based on the average R_o/k ratio for all tests, for each of the three materials. The table also provides the application rate, based on the total mass of material applied to the substrate used in the test chambers. These data show that wood stain has the highest source strength, polyurethane is second, and wood floor wax is lowest. Note that these source strengths do not correspond to the amount of material actually applied.

Table 4. Source strengths and application rates.

Material	Source Strength (mg/m^2)	Application Rate (mg/m^2)
Wood stain	11,800	24,000
Polyurethane	9,000	70,000
Wood floor wax	4,100	5,000

Conclusions

Small test chambers are used to evaluate the emission rate characteristics of building materials, including wood surface treatments. Models are used to fit the chamber data and determine initial emission rates (R_o), emission rate decay (k), and source strength (R_o/k). The effect of air exchange rate (N), as represented by N/L, on R_o and k is shown for three materials. Based on this analysis, increased air exchange rates would increase the emission rates for the wood stain and polyurethane; the floor wax emission rate does not appear to be affected by air exchange rate. The source strength of each material is also presented, with wood stain being the strongest source, followed by polyurethane and floor wax.

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